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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Atmospheric Transformation of Methyl Ethyl Ketone

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The EPA has received a petition to remove methyl ethyl ketone (MEK) from the list of hazardous air pollutants (HAPs). Based on the initial technical review, the review team judged that the estimated MEK concentrations in ambient air are not likely to exceed the EPA's reference concentration (RfC), therefore not likely to result in adverse health effects from direct inhalation exposures. However, MEK is one of many volatile organic compounds (VOCs) that transforms in the atmosphere into acetaldehyde and formaldehyde. These two HAPs are probable human carcinogens and have been identified by the EPA as among the 33 HAPs of greatest concern for the Integrated Urban Air Toxics Strategy published in the Federal Register on July 19, 1999 (64 FR 38706).

The petitioner concludes that insignificant amounts of acetaldehyde and formaldehyde will result from secondary transformation of MEK emissions. This conclusion is based on the premise that MEK has a long half-life (about 9 days) and the transformation products (acetaldehyde and formaldehyde) have short half-lifes, about 14 hours and 3 hours respectively, which means that the transformation products are disappearing much faster than the rate at which they are being formed.

Analyses carried out by Systems Applications International (SAI, an EPA Contractor) as part of the EPA's Cumulative Exposure Project (CEP) identified two pollutants (propene and 2-

butene) as major contributors (or precursors) to ambient concentrations of acetaldehyde and two pollutants (propene and ethene) as major contributors to ambient concentrations of formaldehyde (SAI, 1999). Several other VOCs including MEK were considered minor precursors to acetaldehyde and formaldehyde in the CEP analysis, which provides some additional support for the petitioner's conclusion that MEK transformation is insignificant. However, we determined that further review and analyses were needed to evaluate the transformation of MEK and the petitioner's conclusion.

This memorandum presents an analysis to calculate rough estimates of typical urban ambient air concentrations of acetaldehyde and formaldehyde that could be due to MEK transformation. However, this memorandum does not estimate potential acetaldehyde and formaldehyde levels that could occur near point sources.

Background Information and Input Data:

Methyl ethyl ketone (MEK): C_8H_8O or $C_2H_5COCH_3$

(1) Molecular Weight = 72
(2) Mean ambient air concentration based on available ambient monitoring data from 34 sites in various U.S. urban areas = 1.5 ug/m^3 (U.S. EPA, 1999)
(3) 95 percent ambient air concentration based on available ambient monitoring data from 34 sites in various U.S. urban areas = 4 ug/m^3 (U.S. EPA, 1999)
(4) Half-life = about 9 days = 216 hrs (CARB, 1997)
(5) The major MEK degradation products are acetaldehyde and formaldehyde (CARB, 1997)

Acetaldehyde: C_2H_4O

(1) Molecular Weight = 44
(2) Mean ambient air concentration based on available ambient monitoring data from 73 sites in various U.S. urban areas = 2.5 ug/m^3 (U.S. EPA, 1999)
(3) 95 percent ambient air concentration based on available ambient monitoring data from 73 sites in various U.S. urban areas = 4.5 ug/m^3 (U.S. EPA, 1999)
(4) Half-life = about 15 hrs (CARB, 1997)
(5) EPA's Inhalation Reference Concentration (RfC) = 9 ug/m^3 (U.S. EPA, 1999)
(6) Cancer Inhalation Unit Risk Factor = 0.0000022 per ug/m^3 (U.S. EPA, 1999)
(7) Indoor Air Concentration Range = 5 to 27 ug/m^3 (CARB, 1997)

Formaldehyde: CH_2O

(1) Molecular Weight = 30
(2) Mean ambient air concentration based on available ambient monitoring data from 82 sites in various U.S. urban areas = 2.8 ug/m^3 (U.S. EPA, 1999)

(3) 95 percent ambient air concentration based on available ambient monitoring data from 82 sites in various U.S. urban areas = 5 ug/m^3 (U.S. EPA, 1999)
(4) Half-life = about 3 hrs (CARB, 1997)
(5) Minimal Risk Level (MRL) published by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) = 10 ug/m^3 (ATSDR, 1999). No EPA RfC is available.
(6) Cancer Inhalation Unit Risk Factor = 0.000013 per ug/m^3 (U.S. EPA, 1999)
(7) Indoor Air Concentration Range = 12 to 615 ug/m^3 (CARB, 1997)

General Approach:

The atmospheric chemistry is complex and not fully understood. We assume steady state conditions and no interaction with other atmospheric chemicals. We also assume that the half-life for MEK is 9 days, which is the reported half-life in CARB's Toxic Air Contaminant Identification List Summaries document (CARB, 1997). This analysis is a simplified approach and has significant uncertainties. However, as explained below, we believe this analysis provides conservative (more likely to be overestimated rather than underestimated) rough estimates of the potential acetaldehyde and formaldehyde concentrations and associated risks that could be present in typical urban ambient air due to transformation of MEK.

Expected Ambient MEK Levels and Plume Dispersion:

Since the half-life of MEK is believed to be about 9 days (or 216 hours), we will assume for this ambient air analysis that the plume from any individual point source of MEK is well dispersed before substantial amounts of acetaldehyde or formaldehyde are formed. To demonstrate that this is a reasonable assumption for this analysis, we have conducted a dispersion analysis to show how much a plume of MEK is likely to disperse over time.

To predict what the downwind concentration of a plume might be after 9 days of dispersion (or other durations) we can conduct a simple conservative analysis using the U.S. EPA's SCREEN3 dispersion model. By examining the worst-case facility presented in the petition (IPC in Corninth, MS) and assuming all the facility emissions are emitted from a single low-level point, we can predict what the dispersed concentration would be at a distance well downwind from the plant. If we assume that the average wind speed is about 3 miles per hour (mph), the MEK plume from any given source will travel about 650 miles in 9 days. However, the SCREEN3 model is a gaussian plume model, and is thus only designed to predict plume dispersion out to distances of 100 km (62 miles). Thus, the SCREEN3 model was utilized to predict an ambient concentration from the IPC facility at a distance of 100 km (62 miles), which is about the distance the plume would travel in 21 hours (i.e., about 1/10th the half-life) assuming a 3 mile per hour wind speed. The model predicts a 1-hour MEK concentration of 1.6 ug/m^3 at a distance of 100 km downwind of the facility. During this time period (21 hours or 1/10th the half-life), assuming the half-life of MEK is 9 days, we calculate (using standard decay rate equations) that about 7% (or 0.07) of the MEK would have degraded into acetaldehyde. The

molecular weight (MW) of MEK is 72 and the MW for acetaldehyde is 44. Therefore, we can calculate a concentration of acetaldehyde due to MEK transformation at this point by the following equation:

$[A] = [M] \times 0.07 \times MW_A/MW_M = 1.6\ ug/m^3 \times 0.07 \times 44/72 = 0.07\ ug/m^3$

where, [A] = acetaldehyde concentration
[M] = MEK concentration after 21 hours of dispersion, assuming 3 mph wind
MW_A = molecular weight of acetaldehyde
MW_M = molecular weight of MEK

Using these same calculations for formaldehyde we calculate a concentration of 0.047 ug/m3 formaldehyde after 21 hours of dispersion. However, it's important to note that the above calculation does not account for the fact that acetaldehyde and formaldehyde would be simultaneously degrading as it is being formed. Therefore, the actual acetaldehyde and formaldehyde concentrations due to MEK at this point are expected to be even lower. These calculated acetaldehyde and formaldehyde concentrations after 21 hours of dispersion are well below the mean of the available ambient air monitoring data for acetaldehyde and formaldehyde (presented in the Background section above).

Moreover, when averaged over a longer time period and at the actual distance the plumes have traveled the ambient concentration of MEK from any given source would be expected to be even lower than the SCREEN3 predicted value. Thus, at these distances (650 miles or 62 miles) and these durations (9 days or 21 hours) from any source, it is quite reasonable to assume that the plume would be dispersed many orders of magnitude from its fenceline concentration.

Given the above dispersion analysis and the available ambient monitoring data, we will assume that the 95th percentile of the available ambient air monitoring measurement data for MEK in urban areas (which is 4 ug/m3), is a high-end estimate of the ambient concentration of MEK that would likely exist in a typical urban area.

Rough Estimate of Ambient Acetaldehyde Levels due to MEK transformation:

The half-life of acetaldehyde is about 14 times shorter than the half-life of MEK, which indicates that acetaldehyde degrades about 14 times faster than it is formed from MEK. Based on molecular formulas, it appears that each MEK molecule could form 1 acetaldehyde and 1 formaldehyde molecule. If we assume that each mole of MEK converts to one mole of acetaldehyde and 1 mole of formaldehyde, then we can estimate the resulting acetaldehyde concentrations by the following calculations.

Since, the degradation rate is 14 times greater for acetaldehyde, we will assume that at steady state the number of moles of acetaldehyde per cubic meter of air is 14 times lower than the number of moles of MEK. Since the MW is 1.6 times higher for MEK than for acetaldehyde, the

higher indoor concentrations would also result in higher estimates for cancer risks. However, we judge that it is unlikely that MEK stack or fugitive emissions from industrial sources contributes significantly to these indoor acetaldehyde levels.

What are the estimated levels of formaldehyde due to MEK transformation?

The half-life of formaldehyde is 72 times shorter than the half-life of MEK, which indicates that formaldehyde degrades about 72 times faster than it is formed from MEK. The molecular weight of MEK is about 2.4 times greater than formaldehyde. If we assume that each mole of MEK converts to one mole of acetaldehyde and 1 mole of formaldehyde, then we can estimate the resulting formaldehyde concentrations by the following calculations.

Since, the degradation rate is 72 times greater for formaldehyde, we will assume that at steady state the number of moles of formaldehyde per cubic meter of air is 72 times lower than the number of moles of MEK. Since the MW is 2.4 times higher for MEK than for formaldehyde, the mass of formaldehyde per volume (ug/m^3) will be roughly 173 (i.e., 72 x 2.4) times lower than the mass per volume of MEK. Therefore, assuming steady state, the concentration of formaldehyde (in ug/m^3) is expected to be roughly 173 times lower than the concentration of MEK. Assuming the 95th percentile ambient concentration of MEK of 4 ug/m^3 is a conservative representation of ambient MEK concentrations, we calculate that a conservative estimate for formaldehyde concentrations resulting from these MEK levels would be roughly 173 times lower than the ambient MEK concentration, or 0.02 ug/m^3 (4.0/173.0 ug/m^3).

How much of the ambient formaldehyde concentrations are due to MEK transformation?

Since the ambient average concentration of formaldehyde in urban areas is about 2.8 ug/m^3 (based on available ambient monitoring data for urban areas), we estimate that roughly 0.7% (i.e., 0.02 ug/m^3) of the ambient formaldehyde could be due to MEK transformation. However, we think this is a conservative estimate because we used the **95th percentile** measured MEK ambient level to represent MEK concentrations and the **mean** formaldehyde measured ambient level to represent formaldehyde concentrations. We judge that the actual contribution of MEK to formaldehyde levels in typical urban areas is likely to be less than 0.7%.

What are the estimated risks for formaldehyde exposures?

Using the cancer IURF from IRIS (1.3×10^{-5} per ug/m^3), the upper bound cancer risk due to lifetime exposures to 0.0028 mg/m^3 formaldehyde is estimated to be roughly 3×10^{-5} and the upper bound increased cancer risk due to the fraction that could result from MEK transformation (0.02 ug/m^3) is estimated to be roughly 2×10^{-7} or 2 in 10 million. (The IURF for formaldehyde is currently being reviewed by EPA and is likely to change in the near future. However, we think that the IURF for formaldehyde is not likely to become any higher than the current value, therefore we judge that our estimates for cancer risks for formaldehyde are conservative.)

mass of acetaldehyde per volume (ug/m3) will be 22 (i.e., 14 x 1.6) times lower than the mass per volume of acetaldehyde. Therefore, assuming steady state, the concentration of acetaldehyde (in ug/m3) is expected to be roughly 22 times lower than the concentration of MEK. Assuming the 95th percentile of the ambient concentration data for MEK of 4 ug/m^3 is a conservative representation of ambient MEK concentrations that would be expected in typical urban areas, we calculate that a conservative estimate for acetaldehyde concentrations resulting from degradation of these MEK levels would be roughly 22 times lower, or 0.18 ug/m3 (4.0/22.0 ug/m3).

How much of the ambient acetaldehyde concentrations are due to MEK Transformation?

Since the ambient average concentration of acetaldehyde in urban areas is about 2.5 ug/m^3 (based on available ambient monitoring data for urban areas), we estimate that roughly 7% (i.e., 0.18 ug/m3) of the ambient acetaldehyde could be due to MEK transformation. However, we think this is a conservative estimate because we used the **95th percentile** measured MEK ambient level to represent MEK concentrations and the **mean** acetaldehyde measured ambient level to represent acetaldehyde levels. We judge that the actual contribution of MEK to acetaldehyde levels in typical urban areas is likely to be less than 7%.

What are the potential risks to humans due to these acetaldehyde concentrations?

To evaluate the potential risks for public health, the increased cancer risks can be estimated. Using EPA default exposure and risk assumptions (such as the assumptions that there is no threshold for the carcinogenic effect and the dose-response relationship is linear at low doses) the increased risk of cancer for people assumed to be exposed for a lifetime to the ambient concentration can be calculated by multiplying the ambient concentration by the Cancer Inhalation Unit Risk Factor (U.S. EPA 1986, U.S. EPA 1998a, U.S. EPA 1997 and U.S. EPA 1998b). The Cancer Inhalation Unit Risk Factor (IURF) is an upper bound estimate of the increased risk of cancer per unit of exposure. The IURF for acetaldehyde is 2 x 10^{-6} per microgram per cubic meter (per ug/m^3). This means that if people are exposed to 1 microgram of acetaldehyde per cubic meter of air (1 ug/m^3) for a lifetime we estimate that they would have an estimated upper bound increased risk of cancer of 2.2 x 10^{-6}, or 2.2 in 1 million. Therefore, if we assume people are exposed to the average ambient concentration of acetaldehyde (i.e., 2.5 ug/m^3) for a lifetime, we calculate the upper bound increased cancer risk for these people to be about 6 in 1 million, or 6 x 10^{-6}. Using the same type of calculation, we estimate the upper bound increased risk of cancer due to the fraction of acetaldehyde that could result from MEK emissions transformation alone (i.e., 7% or 0.18 ug/m^3), to be roughly 4 in 10 million, or 4 x 10^{-7}.

Potential for noncancer risks can also be evaluated. The RfC for acetaldehyde is 9 ug/m^3, which is higher than the ambient concentrations reported above, therefore, adverse noncancer effects are not expected to occur due to exposures to these outdoor ambient concentrations. However, higher levels could occur near sources directly emitting acetaldehyde, which were not assessed in this analysis. Also, indoor air levels of acetaldehyde (see background information above) can be higher than outdoor air. These indoor air levels could easily exceed the RfC. The

With regard to noncancer effects, we will compare ambient levels to the minimal risk level (MRL) for formaldehyde, which is 10 ug/m^3 (ATSDR 1999). The ambient levels of formaldehyde used for this analysis are less than the MRL, which suggests that adverse noncancer effects are not likely to result due to exposures to these outdoor levels. However, higher levels could occur near sources directly emitting formaldehyde, which were not evaluated in this assessment. Also, higher levels occur indoors (see above), which may pose concerns for potential noncancer effects. However, we judge that stack and fugitive MEK emissions from industrial sources are not likely to contribute significantly to these indoor formaldehyde levels.

Combined cancer risks of acetaldehyde and formaldehyde formation from MEK:

To determine the total increased cancer risk that could result due to MEK emissions transformation, we will assume that cancer risks are additive, which is consistent with EPA guidelines (U.S. EPA 1986). Following this approach, we add the estimated increased cancer risk for the acetaldehyde fraction due to MEK transformation (i.e., risk of 4×10^{-7}) and for formaldehyde (i.e., 2×10^{-7}). This results in an estimated cumulative upper bound increased cancer risk due to MEK emissions transformation of 6 in 10 million, or 6×10^{-7}.

Uncertainties about the estimated half-life for MEK:

In the above calculations, we assumed that the half-life of MEK was 9 days based on the value presented in CARB, 1997. There are uncertainties in this value. The actual half-life could be lower or higher than 9 days depending on meteorology, sunlight, presence of other atmospheric pollutants and constituents, and other factors. However, we believe that a half-life of 9 days is a reasonable value for this assessment.

Conclusions:

The quantitative risk estimates presented above are uncertain due to the simplified approach, assumptions made, and incomplete knowledge of the atmospheric chemistry and toxicity of the chemicals. However, we generally used conservative assumptions including the following: lifetime exposures; linear non-threshold dose-response relationship; and that the 95th percentile of the MEK ambient measurement data represents the ambient MEK concentrations. Therefore, we judge that the estimates of increased cancer risk due to MEK transformation presented in this analysis are more likely to be overestimated rather than underestimated. Overall this analysis suggests that the fractions of acetaldehyde and formaldehyde in typical urban ambient air resulting from transformation of MEK emissions are not likely to pose increased cancer risks greater than 1 in 1 million, or 1×10^{-6}. Also, we judge that noncancer risks due to MEK transformation are not likely to be significant.

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